

nary temperatures. It condenses to a colorless liquid boiling at -16.1° and freezes to a white solid at -135.8° .

Both of these compounds hydrolyze on contact with the moisture in the air, react with mercury,

liberating phosphorus, combine with bromine to form unstable compounds, probably PFBr_4 and PF_2Br_3 , and decompose slowly forming PF_3 and PBr_3 at dry-ice temperatures (-78°).

CLEVELAND, OHIO

RECEIVED AUGUST 9, 1939

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

The Fluorination of Phosphoryl Trichloride

BY HAROLD SIMMONS BOOTH AND FREDERIC B. DUTTON¹

Booth and Swinehart² have shown that antimony trifluoride in the presence of a catalyst such as antimony pentachloride causes the progressive fluorination of inorganic non-polar halides. The present investigation is a study of the fluorination of phosphoryl chloride. Phosphoryl trifluoride had been prepared, and its properties first described by Moissan³ by sparking a mixture of phosphorus trifluoride and oxygen. It has been prepared since by a number of workers using different methods.⁴ The intermediate chlorofluorides have not been described previously.

Preparation of Phosphoryl Chlorofluorides.—Phosphoryl trichloride was fluorinated by means of antimony trifluoride using antimony pentachloride as a catalyst, and by means of calcium fluoride pellets at elevated temperatures. The apparatus used in these experiments has been described by Booth and Bozarth.⁵

Fluorination with Calcium Fluoride.—Fluorination by means of calcium fluoride was effected by passing the vapor of boiling phosphoryl trichloride over calcium fluoride pellets contained in an electrically-heated glass tube. The gases on leaving the reactor were so separated in a fractionating column that any unreacted material was returned to the boiling chamber and the fluorinated products were removed continuously. A generation carried out at a pressure of 100 mm. and with the reactor column containing the calcium fluoride pellets held at a tempera-

ture of 200° yielded about 90% phosphoryl trifluoride and 10% of higher-boiling substances. A generation carried out at 150° yielded about 35% of the trifluoride, 25% difluoromonochloride, and 40% monofluorodichloride. A generation at 120° gave chiefly the trifluoride but soon stopped and could be continued only by raising the temperature.

Fluorination with Antimony Trifluoride.—Fluorination by means of antimony trifluoride was carried out by slowly adding resublimed, finely crystalline antimony trifluoride⁶ to a mixture of 200 g. of phosphoryl trichloride and 50 g. of antimony pentachloride while the liquid mixture was stirred rapidly and maintained at a predetermined temperature. The volatile products of the reaction passed through a condenser which was cooled by running water at about 10° .

A generation carried out with the reaction flask at 75° and a pressure of 190–200 mm. yielded about 55% of phosphoryl trifluoride, 5% of difluoromonochloride and 40% of monofluorodichloride. Higher temperatures (up to the boiling point of phosphoryl trichloride) did not seem to alter the above ratio and lower temperatures increased the yield of the trifluoride at the expense of the other products. The fluorinated products were fractionally distilled in a column, rapidly at first, to effect rough separation of the components. Each component was then carefully refractionated two or more times until further fractionation produced no change in the melting point.

Identification of the Phosphoryl Fluorochlorides

Analysis.—Samples for analysis were condensed in heavy walled bulbs connected to the apparatus by flat-joint connections. After filling, the bulbs were sealed off, weighed, frozen, the necks broken and all dropped into half-normal alkali. The gases dissolved completely on warming. Chlorine was determined either gravimetrically or by the Volhard method, and phosphorus by precipitation as the phosphomolybdate and twice as magnesium ammonium phosphate before ignition to the pyrophosphate.

No particular difficulty was encountered in the analysis of phosphoryl monofluorodichloride or the difluoromonochloride, but phosphoryl trifluoride gave results at first 2–4% low and it was found necessary to evaporate the acidified sample to dryness in a platinum dish to decompose fluophosphates before proceeding with the analysis.

(6) Kindly furnished by the Harshaw Chemical Company, Cleveland, Ohio.

(1) Submitted by Frederic B. Dutton to the Graduate School, Western Reserve University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, May, 1937. Reported at the Rochester Convention of the American Chemical Society, September 10, 1937. Original manuscript received August 24, 1938.

(2) H. S. Booth and C. F. Swinehart, *THIS JOURNAL*, **54**, 4751 (1932).

(3) H. Moissan, *Compt. rend.*, **99**, 655 (1884).

(4) H. Moissan, *ibid.*, **102**, 1245 (1886); H. Moissan, *Bull. soc. chim.*, [3] **4**, 260 (1890); *ibid.*, [3] **5**, 456 (1891); *ibid.*, [3] **5**, 458 (1891); H. Schulze, *J. prakt. Chem.*, [2] **21**, 443 (1880); Thorpe and Hambly, *J. Chem. Soc.*, **55**, 759 (1889); A. Guntz, *Compt. rend.*, **103**, 58 (1886); C. Poulenc and H. Moissan, *ibid.*, **113**, 75 (1891).

(5) H. S. Booth and A. R. Bozarth, *Ind. Eng. Chem.*, **29**, 470 (1937); *THIS JOURNAL*, **61**, 2927 (1939). Additional illustrations and descriptions of this type of apparatus have been given by H. S. Booth and C. V. Herrmann, *ibid.*, **58**, 63 (1936); H. S. Booth and W. C. Morris, *ibid.*, **58**, 90 (1936).

TABLE I

	Phosphorus			Chlorine			Gas density	
	Calcd.	by CaF ₂	by SbF ₃	Calcd.	by CaF ₂	by SbF ₃	Calcd.	Found
POFCl ₂	22.65	22.63	22.31	51.79	51.36	51.97		
		22.67	22.61		51.49	51.97		
POF ₂ Cl	25.75	25.08	25.39	29.43	29.37	29.54	120.5	119.7
		24.85	25.24		29.65	29.54		
POF ₃	29.82	30.07	30.02				104.0	103.4
			29.25					

The gas densities of the phosphoryl trifluoride and difluoromonochloride were determined in a gas density balance as described by Booth and Bozarth.⁵

Physical Properties

Freezing Points.—Freezing points were determined as usual in this Laboratory in a cell containing a magnetic stirrer and a thermocouple, surrounded by two or three concentric glass jackets and finally a Dewar jar containing liquid air. The temperatures were measured by a three-junction thermocouple. The fixed junction was held at the temperature of melting ice and the cooling curves automatically recorded on a Leeds and Northrup Micro-max recording potentiometer. Considerable difficulty was encountered in melting and freezing phosphoryl trifluoride. Moissan gave as the boiling point -40° , which is essentially correct, and as the melting point -65° , which is seriously in error. The best determination made in this investigation put the freezing point at -39.4° .⁷ The vapor pressure of the solid at the melting point is 771 mm. The liquid has a tendency to superheat with the resulting sudden increase in pressure which either blows a manometer, breaks the apparatus, or both.

On several occasions, when phosphoryl trifluoride had been condensed with liquid air as the refrigerant and this was later changed to dry-ice, the ampoule or cell holding the trifluoride cracked. It was thought that this phenomenon might be the result of a conversion of one solid modification to another. An attempt was made to discover the presence of a transition point by studying the vapor pressure of the solid but it was found that phosphoryl trifluoride condensed with liquid air and then held in dry-ice required two or three days to come to equilibrium, rendering it impractical to make a series of observations of the vapor pressure of the solid at different temperatures.

A second attempt to locate such a transition point was made by the differential method.⁸ About 15 cc. of liquid phosphoryl trifluoride was frozen in the bottom of a cell which contained a copper neutral body just above the frozen gas. Two thermocouple wells entered the cell, one terminating in the neutral body and the second at the center of the frozen gas. The entire cell was cooled to liquid air temperature and a warming curve taken. The temperature was observed on the recording potentiometer by means of a 3-junction thermocouple using dry-ice as

the fixed junction. At the same time the differential temperature between the neutral body and the frozen gas was observed on a second recording potentiometer by means of a 3-junction thermocouple. The warming curve indicated a change in the rate of warming and the differential curve indicated a maximum at approximately -100° , but neither curve showed a "sharp break"; this indicates a slow transition from one form to another.

TABLE II

Temp., °C.	VAPOR PRESSURE OF POFCl ₂		Deviation, mm.
	P, obsd., mm.	P, calcd., mm.	
-30.0	14.6	15.4	0.8
-30.0^a	14.6	15.4	.8
-20.0	28.1	28.2	.1
-20.0^a	28.1	28.2	.1
-10.0	48.8	49.4	.6
-10.0^a	49.4	49.4	.0
0.0	84.8	82.9	-1.9
0.0	83.7	82.9	-0.8
10.0	136.5	134.2	-2.3
20.0	216.1	210.4	-5.7
20.0 ^a	217.0	210.4	-6.6
21.2 ^a	227.6	221.6	-6.0
25.0	266.9	260.4	-6.5
30.0	326.5	320.0	-6.5
40.0	480.9	473.8	-6.2
49.8	683.1	678.4	-4.7
53.1	764.7	764.2	-0.5
54.9	813.4	813.6	0.2
59.3	942.7	945.6	2.9

^a Prepared by Swarts reaction; all others by reaction with calcium fluoride. Calculated values were determined by use of the equation $\log p = (-1618.23/T) + 7.8440$.

Vapor Pressure.—The vapor pressure data for phosphoryl monofluorodichloride, which is a liquid at room temperature, were determined in the isotenscope described by Booth, Eley and Burchfield.⁹ The vapor pressure data for the gases phosphoryl difluoromonochloride and trifluoride were obtained by direct observation of the pressure of the respective liquids held in small glass bulbs, immersed in a thermostat. Temperatures were measured by a resistance thermometer calibrated by the U. S. Bureau of Standards.

(7) Dr. G. Tarbuton, Department of Chemical Engineering, Tennessee Valley Authority, Wilson Dam, Alabama, has found the freezing point of phosphoryl trifluoride to be -39.1° .

(8) G. K. Burgess, *Bull. Bur. Standards*, **5**, 199 (1908).

(9) H. S. Booth, H. M. Eley and P. E. Burchfield, *THIS JOURNAL*, **57**, 2064 (1935).

TABLE III
 VAPOR PRESSURE OF POF_2Cl

Temp., °C.	P, obsd., mm.	P, calcd., mm.	Deviation, mm.
-62.1 ^a	18.9	24.8	6.1
-55.4 ^a	30.9	38.8	7.9
-40.2	98.5	97.1	-1.4
-31.1	153.5	159.1	5.6
-20.9	264.4	265.2	0.8
-13.6	376.5	373.1	-3.4
-12.2	397.5	397.4	-0.1
-9.3 ^a	444.4	452.1	7.7
-5.2	543.2	539.9	-3.3
-0.1 ^a	665.4	668.2	2.8
-0.1	677.2	668.2	-9.0
1.2 ^a	700.0	704.5	4.5
2.2	737.8	733.7	-4.1
6.4 ^a	864.6	867.0	2.4
11.3 ^a	1047.3	1047.0	0.0
15.1 ^a	1206.1	1206.0	0.0

^a Prepared by Swarts reaction: all others by calcium fluoride. Calculated values were determined by use of the equation $\log p = (-1328.3/T) + 7.6904$.

 TABLE IV
 VAPOR PRESSURE OF POF_3

Temp., °C.	P, obsd., mm.	P, calcd., mm.	Deviation, mm.
-43.8 ^a	637.7	627.9	-9.8
-42.7 ^a	670.0	668.2	-1.8
-41.6 ^a	701.9	704.0	2.1
-40.2	758.1	751.8	-6.3
-38.9 ^a	798.9	798.6	-0.3
-38.4	813.6	817.0	3.4
-37.3	862.3	859.2	-3.1
-35.9	912.5	915.4	2.9
-35.4 ^a	942.5	936.1	-6.4
-35.2	954.1	946.3	-7.8

^a Prepared by Swarts reaction: all others by calcium fluoride. Calculated values were determined by use of the equation $\log p = (-1097.88/T) + 7.5900$.

Critical Constants.—The critical constants and vapor pressure of phosphoryl trifluoride at high pressures were determined in the apparatus of, and as described by, Booth and Swinehart.¹⁰ No

 TABLE V
 CRITICAL DATA

Sam- ple	POF_3		POF_2Cl	
	Temp., °C.	Pressure, atm.	Temp., °C.	Pressure, atm.
1	24.9	12.5		
2	35.8	17.0		
1	40.3	19.1		
2	48.8	24.3		
1	59.9	30.9		
2	68.1	38.8		
1	73.3	41.7	150.5	43.4
2	73.3	41.9	150.8	43.5

(10) H. S. Booth and C. F. Swinehart, *THIS JOURNAL*, **57**, 1337 (1935).

difficulty was encountered with the trifluoride, but the difluoromonochloride reacted slowly with the mercury.

Chemical Properties.—The properties of the phosphoryl fluorochlorides lie between those of the trichlorides and the trifluorides, and are proportional to the fluorine content. They hydrolyze in moist air or water with increasing rapidity, although the hydrolysis of the compounds containing fluorine is complicated by the intermediate formation of fluophosphates.

 TABLE VI
 PHYSICAL PROPERTIES OF THE FLUORINATION PRODUCTS OF POCl_3

	POF_3	POF_2Cl	POFCl_2
Boiling point, ^a °C.	-39.8 ± 0.1	3.1 ± 0.1	52.9 ± 0.1
Freezing point, °C.	-39.4	-96.4	-80.1
Liquid density (at 0°)		1.6555	1.5931
Gas density	104.0	120.5	
Critical temperature, °C.	73.3	150.6	
Critical pressure, atm.	41.8	43.4	
Heat of vaporization, ^b cal.	5030	6090	7403
Trouton's constant	21.6	22.03	22.7

^a From a plot of the vapor pressure data. ^b Calculated by the Clausius-Clapeyron equation.

All four substances are colorless in all states. All three fluorination products have little or no action on nichrome and copper. The trifluoride and the difluoromonochloride have a slight tendency to discolor the surface of mercury after prolonged exposure. When dry, the gases do not attack glass, but no precautions in the way of preliminary drying were sufficient to prevent the formation of a white ring at the surface and a slight cloudiness in the bottom of the container whenever the material was condensed in glass. This is most marked with the trifluoride and the difluoromonochloride and is very slight with the monofluorodichloride.

Phosphoryl difluoromonochloride was passed over sodium amalgam both in the gaseous and liquid states, in an attempt to remove the chlorine and form a condensation product of the formula $(\text{POF}_2)_2$. The surface of the amalgam was discolored, but there was no further evidence of reaction in the range of 20–60°.

Summary

The fluorination of phosphoryl trichloride by the Swarts reaction, and in the vapor phase by calcium fluoride pellets, yields two gases, phosphoryl trifluoride boiling at -39.8° first described

by Moissan, phosphoryl difluoromonochloride boiling at 3.1° and a liquid, phosphoryl monofluorodichloride boiling at 52.9°. The freezing points, vapor pressure data, critical constants, gaseous and

liquid densities have been determined and recorded along with a few of their chemical properties.

CLEVELAND, OHIO

RECEIVED AUGUST 9, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Entropy of Cyanogen. Heat Capacity and Vapor Pressure of Solid and Liquid. Heats of Fusion and Vaporization

BY R. A. RUEHRWEIN AND W. F. GIAUQUE

This paper is a report on a low temperature calorimetric investigation on solid and liquid cyanogen, $N\equiv C-C\equiv N$. The results have been used to calculate the entropy of the gas by means of the third law of thermodynamics and this value has been compared with one calculated from available molecular data. The two values agree within their respective limits of error.

The measurements were made in a calorimeter with the laboratory designation Gold Calorimeter III and temperatures were obtained by means of Standard Copper-Constantan Thermocouple W-25, both of which have been described previously.^{1,2}

Preparation and Purity of Cyanogen.—Cyanogen was prepared by a method similar to one described by Cook and Robinson.³ Silver cyanide was precipitated from a saturated silver nitrate solution by a slight excess of a 78% solution of potassium cyanide. The silver cyanide was filtered, washed free of excess cyanide and dried in an oven at 130° for twelve hours. The silver cyanide prepared in this way was a pale brown powder. It was then heated in a glass vessel and a temperature of approximately 380° was maintained.

The cyanogen, which was evolved steadily at a pressure of about half an atmosphere, was passed through two tubes containing phosphorus pentoxide and finally condensed in a bulb surrounded by liquid air but protected from it in case of breakage. The phosphorus pentoxide tubes were 3 cm. in diameter and 30 cm. long. The preparation system was evacuated to a pressure of 10^{-5} mm. before the cyanogen was generated; 180 cc. of liquid was prepared. The material was distilled twice, small end-fractions being discarded, and

the solid was subjected to a high vacuum to remove any non-condensable gases; 135 cc. of liquid remained after this treatment.

From the effect of premelting on heat capacity measurements below the melting point the liquid-soluble solid-insoluble impurity was estimated to be 5 parts in 100,000 on a molal basis.

The Melting Point of Cyanogen.—A summary of the melting point investigation is given in Table I.

TABLE I
MELTING POINT OF CYANOGEN
0°C. = 273.10°K.

Time	% melted	T, °K. Resistance thermometer	T, °K. Thermo- couple
7-27-38			
5:34 P. M.	Heated into melting point		
5:45 P. M.	10	245.281	245.26
8:25 P. M.	10	245.275	245.25
10:00 P. M.	10	245.265	245.27
11:12 P. M.	Supplied heat		
11:30 P. M.	40	245.264	245.30
7-28-38			
11:10 A. M.	40	245.278	245.27
12:08 P. M.	40	245.270	245.27
1:23 P. M.	Supplied heat		
1:45 P. M.	70	245.277	245.28
3:45 P. M.	70	245.269	245.27
5:35 P. M.	70	245.272	245.27
		Accepted value	245.27

The Vapor Pressure of Cyanogen.—The vapor pressure was measured with a Société Gènevoise cathetometer with a precision of 0.002 cm. It was used as a comparison instrument for a standard meter suspended between the arms of the manometer, which was protected by a case with uniform temperature. The standard acceleration of gravity was taken as 980.665 cm. sec.⁻² and the acceleration at this location as 979.973 cm. sec.⁻². Data given in the "I. C. T."⁴

(1) Giauque and Egan, *J. Chem. Phys.*, **5**, 47 (1937).

(2) Giauque and Ruehrwein, *This Journal*, **61**, 2626 (1939)

(3) Cook and Robinson, *J. Chem. Soc.*, 1001 (1935).

(4) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1926, Vol. I.